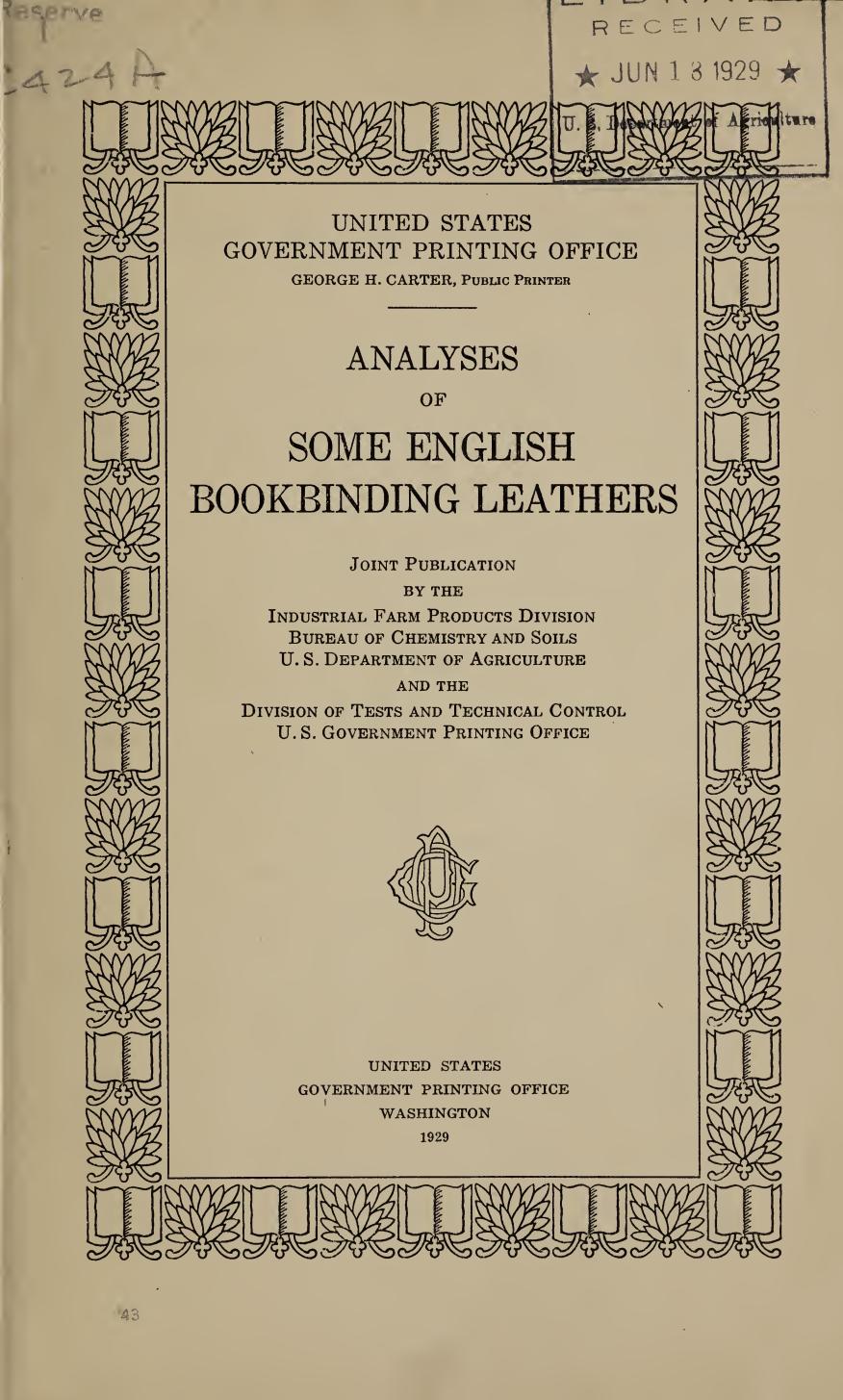
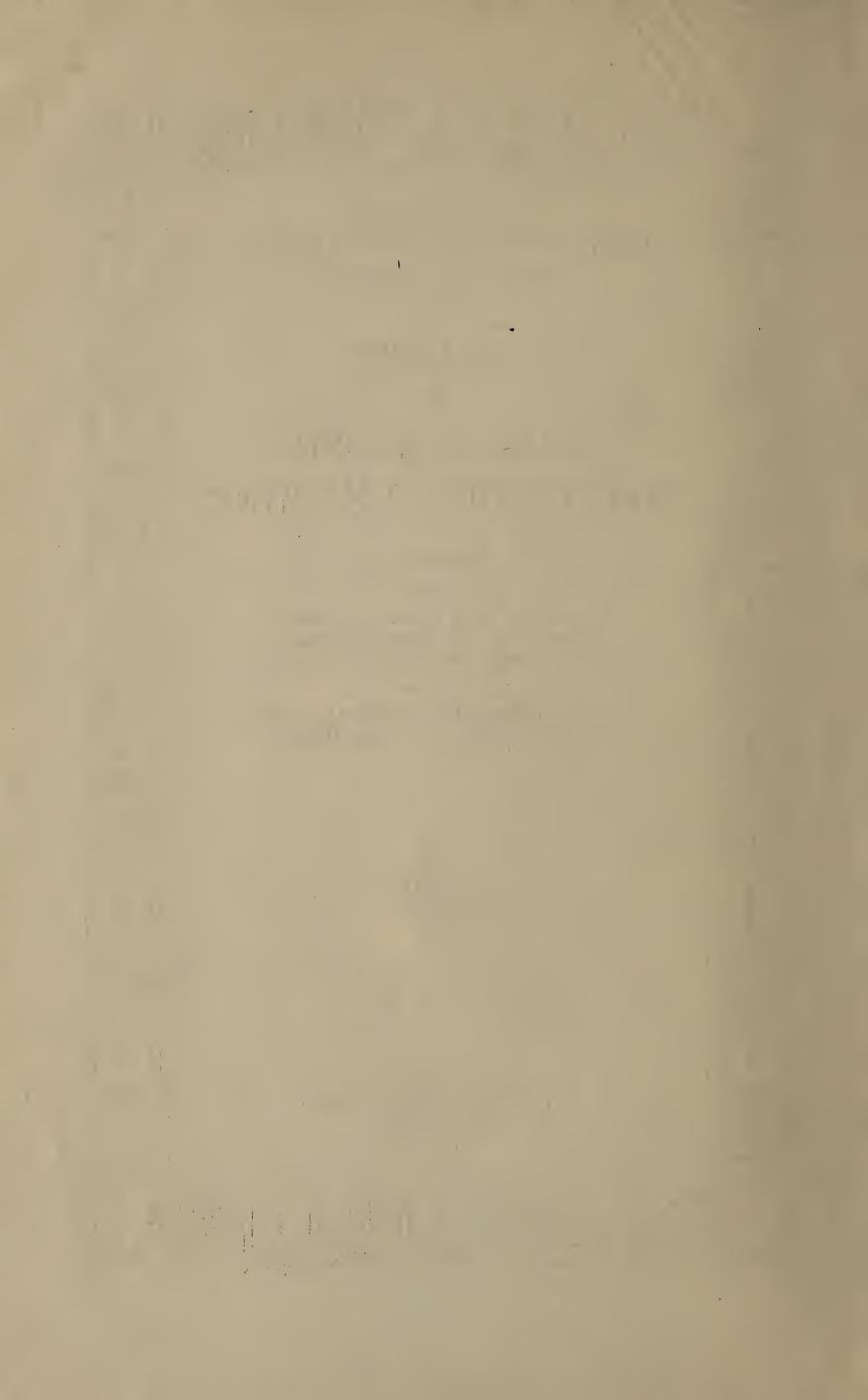
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# ANALYSES OF SOME ENGLISH BOOKBINDING LEATHERS

By R. W. Frey, L. R. Leinbach, and E. O. Reed 3

The report of one of the most comprehensive investigations ever conducted on bookbinding leather was published in 1901 by the Committee of the Royal Society of Arts on Leather for Bookbinding. This report pointed out some of the causes for the rapid deterioration of leather bindings and made a number of recommendations regarding the essential requirements for the production of serviceable and durable bookbinding leathers. These recommendations have been ignored entirely or in part by many tanners of bookbinding leather, with the result that deterioration and failure of leather bindings dating since 1900 are still common. The failure of leather bindings to render long service, together with the high initial cost of leather as compared with other bookbinding materials, is bringing about a widespread substitution of bookbinding cloths of various types and of cellulose-coated fabrics. Because of its inherent properties, however, leather offers admirable and unique possibilities as a bookbinding material, and when properly prepared and tanned for the purpose should find but few serious competitors.

The subject of desirable bindings has long been of keen interest to both the United States Department of Agriculture and the United States Government Printing Office, especially to the latter because it is a large consumer of bookbinding materials. For bindings intended for long service, such as those for records and for reference works, the necessity of using only leathers of the best quality and tannage is fully appreciated. Much attention has been given, therefore, to obtaining data for the preparation of suitable specifications and to locating sources of the most suitable leathers.

In 1926, the technical director of the Government Printing Office obtained directly from three English tanners a number of bookbinding leathers of good quality for use in investigational work on this subject. Each sample consisted of a whole skin. Most of the leathers were

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4 Report of the Committee of the Society of Arts on Leather for Bookbinding. London, England, 1901.

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claimed to have been made in accordance with the recommendations contained in the Report of the Committee of the Royal Society of Arts on Leather for Bookbinding.

Several series of books have been bound in these leathers and placed in different Government libraries in Washington to obtain service records on them. Data on the physical and chemical properties of these leathers, for correlation with their service records, have been obtained by the Industrial Farm Products Division, Bureau of Chemistry and Soils, United States Department of Agriculture, which division has been in close and active cooperation with the Government Printing Office in all its investigational work on bookbinding leather. These data are presented herewith not only for record but especially for the information of tanners and buyers of bookbinding leather.

#### PHYSICAL EXAMINATION

Physical measurements, including determination of the weight per unit area and the average thickness, and chemical analysis were made of each leather on a section extending 10 inches along the backbone line from the root of the tail and 8 inches at right angles to this line.

Although this test section may not be strictly representative of a whole skin or side, it was considered a sufficiently definite and representative sample to give for practical purposes comparable results for leathers made from any one kind of hides or skins.

Six strips were taken from each section for strength and stretch tests. Three were cut parallel to the backbone line, and three were cut in the opposite direction. Figure 1 shows the location of the test section and the test pieces.

The test strips were cut with a round-shoulder die having a restricted or test area 5 centimeters long and 1 centimeter wide. They were conditioned at 50 per cent relative humidity and 70° F. and broken at this humidity and temperature by a vertical, tensile-strength tester of the inclination-balance type. The tester was motor driven. The rate of separation of the jaws of the tester was 36 centimeters, or 14 inches per minute.

Table 1 and 2 show the results of the physical examination. In Table 1 the figures for strength and stretch are average results on the six test pieces of each sample. Strength is given as the calculated breaking load for both unit width of the leather and unit cross-section area. Stretch is given as the per cent elongation of the leather at the breaking load. In Table 2 average strength and stretch results on the strips cut parallel to the backbone line and those cut at right angles to it are given separately.

The leathers showed marked variation in strength. Of the 13 goatskin leathers, 2 had a breaking strength per square inch cross section of 3,000 pounds or more; 2, between 2,500 and 3,000 pounds; 6, between 2,000 and 2,500 pounds; and 3, less than 2,000 pounds. Of the 6 calfskin leathers, 3 had a breaking strength of more than 3,500 pounds per square inch; 1, 2,500 pounds; and 2, less than 2,000 pounds.

Although of questionable significance, it is interesting to find by comparison with the data on chemical analysis in Table 3 that of the 5 leathers having a strength of less than 2,000 pounds 4 showed acidity of 0.5 per cent or more; of the 10 leathers having a strength between 2,000 and 2,500 pounds but 3 showed acidity of 0.5 per cent or more; and of the remaining 8 leathers having a breaking strength

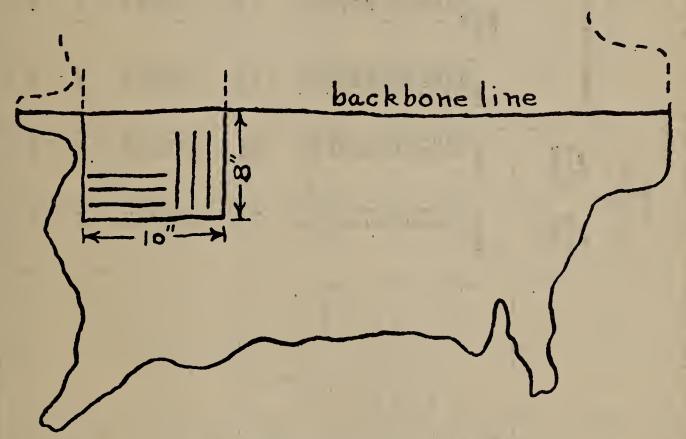


Fig. 1.—Location of test section and test pieces

in excess of 2,500 pounds 7 showed no acidity, and the other showed an acidity of 0.3 per cent.

The data in Table 2 show no consistent relationship between strength and direction in the skin, for from a total of 23 leathers, 12 had a greater strength in the direction at right angles to the backbone line and 11 a greater strength in the opposite direction. From these results it would appear that generalizations can not be made with regard to the strength of leather and direction in the skin or hide.

In some of the leathers the strength in the two directions differed widely. For example, for leathers 1, 2, 4, 7, 9, 12, and 15 the average breaking strength in one direction ranged from only 47 per cent to 70 per cent of the strength in the opposite direction.

Table 1.—Average weight, thickness, strength, and stretch of the leathers

		A verage stretch	Per cent 50 61 82 83 83 84 85 84 85 84 85 84 85 85 85 85 85 85 85 85 85 85 85 85 85	57 55	35.22 37.33 38 38.33 38.33 38.33 38.33 38.33 38.33 38.33 38.33 38.33 38.33 38	20	18
	A verage strength	Per square centi- meter cross section	Kilo- grams 156 120 134 194 115 123 175 123 175 175 175 175 175 175	151	178 250 258 140 140 114	152	154
		Per square inch cross section	Pounds 2, 218 1, 706 2, 759 2, 759 1, 749 2, 489 2, 247 2, 247 2, 247	2, 147 2, 161	2, 531 3, 555 3, 669 1, 991 1, 621	2, 161	2,190
		Per centi- meter width	Kito- grams 11. 3 9. 7 16. 0 17. 6 17. 8 11. 8 11. 8 11. 7 11. 8 11. 7 11. 8 11. 7 11. 8 11. 7	11.8	15.6 28.0 25.5 9.6 6.0	15.2	12.4
o logicanos	orx I	Per inch width	Pounds 63.3 54.3 89.6 88.7 71.1 775.0 110.9 105.8 75.6 93.0	66.1 65.0	27.4 142.8 53.8 33.6	85.1	69.4
5		Average thickness	Milli- meters 0.74 .76 1.09 .91 .91 .91 .91 .94 .94	.81		1.07	. 79
-		A verage	Inch 0.029 0.029 0.030 0.036 0.036 0.036 0.033 0.037	.031	. 036 . 039 . 025 . 020 . 021	. 042	.031
TABLE 1. True age weight, interitors, with survey of the teamers	Weight	Per square meter	Grams 458 473 732 671 580 580 580 580 580 580 610 641	519	595 778 702 458 336	732	549
	Wei	Per square foot	Ounces 1.5- 1.52.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2	1.7	1111222	2.4	1.8
i. tree age weight,		Description	Law goat, sumac tanned, whole binding <sup>1</sup> Law goat, sumac tanned, half binding <sup>1</sup> Crimson Cape, whole binding, dull grain <sup>1</sup> Crimson Cape, half binding, dull grain <sup>1</sup> Crimson Cape, half binding, dull grain <sup>1</sup> Natural Niger goat, dull scarlet Red sumac goat. Green, hard grain, Morocco Green Morocco, sumac tanned, pebbled <sup>1</sup> Brown Morocco, sumac tanned, pebbled <sup>1</sup> Blue Morocco, sumac tanned, pebbled <sup>1</sup> Blue Morocco, sumac tanned, pebbled <sup>1</sup> Blue Morocco, sumac tanned, pebbled <sup>1</sup>	Red roan Law sheep, sumac tanned 1	Law calf.  Blue calf, sumac tanned, whole binding 1.  Blue calf, sumac tanned, half binding 1.  Brown, bark calf.  Natural, bark calf.  Blue, sumac calf.	Red Russia	Red pigskin
		Tan- ner	4444mm0000000	, M 4	M44000	Ö	м
-		Leather	11. 11. 13. 11. 13.	15	16 17 18 19 20 21	22	23-

1 Labeled either "No mineral acids" or "Free from injurious acids."

Table 2.—Average strength and stretch of the leathers with respect to direction in the skin

			Average	Average stretch			
Leather	Tan-	Parallel bone	to back-	At right backbo	angles to one line		At right angles to backbone line
	ner	Per square inch cross section	Per square centime- ter cross section	Per square inch cross section	Per square centime- ter cross section	Parallel to back- bone line	
GOATSKIN  1	AAAABBCCCCCCC	Pounds 1, 550 1, 181 2, 162 3, 271 3, 143 1, 806 1, 124 2, 603 2, 574 3, 485 3, 101 1, 849 2, 489	Kilograms 109 83 152 230 221 127 79 183 181 245 218 130 175	Pounds 2, 887 2, 233 2, 347 2, 233 2, 375 1, 991 2, 361 2, 361 1, 877 3, 257 2, 901 2, 645 2, 205	Kilograms 203 157 165 157 167 140 166 166 132 229 204 186 155	Per cent 50 56 33 29 26 26 27 36 30 39 40 29 28	Per cent 50 65 31 26 48 21 51 53 55 63 58 59 52
SHEEPSKIN  14	B A	2, 048 1, 778	144 125	2, 247 2, 546	158 179	43 46	71 63
CALFSKIN  16	B A C C C	2, 247 3, 911 3, 812 1, 892 3, 883 1, 764	158 275 268 133 273 124	2, 802 3, 328 3, 527 2, 091 3, 641 1, 479	197 234 248 147 256 104	42 32 33 36 34 28	41 35 30 34 39 48
COWHIDE 22	С	1, 892	133	2, 418	170	26	26
PIGSKIN 23	В	2, 119	149	2, 247	158	16	19

### CHEMICAL ANALYSIS

The broken test pieces and the remainder of the test section were prepared for chemical analysis by being cut into small pieces ranging from one-eighth to one-quarter of an inch square.

Except for the determination of water solubles, the samples were analyzed according to the official methods of the American Leather Chemists Association, which specify petroleum ether for the extraction of fats and the Proctor and Searle procedure for the determination of acidity. Water solubles were determined in an extract made by soaking 15 grams of leather in water at laboratory temperature overnight and then extracting to 1 liter in three hours by percolation with water at 50° C. pH values were obtained electrometrically with the hydrogen electrode on parts of the water extract made for water solubles. The nature of the tannin material was determined by the response of parts of the water extract to the usual tests with bromine water, iron alum, and formaldehyde and hydrochloric acid. Table 3 gives the results of the chemical analysis on the moisture-free basis.

Table 3.—Chemical analysis of the leathers [Results on moisture-free basis]

Nature of tanning material	Pyrogallol.	Do. Do.	Do. Mixture catechol and pryogallol. Pyrogallol.	0.00	Do:	Do. Do.		Mixture catechol and pyrogallol. Pyrogallol.	Mixture catechol and pyrogallol. Pyrogallol.	Do. Do. Mixture catechol and pyrogallol. Pyrogallol.	Mixture catechol and pyrogallol.	Mixture catechol and pyrogallol.
pH of water extract	3,3	.3.6 3.9	&4; ₩4; ₩6; ₩6; ₩6; ₩6; ₩6; ₩6; ₩6; ₩6		3. 7.	3.6		 	33.3	6.6.4.0.0 0.4.1.0	2.4	2.9
Acidity, Proctor &	Per ct.	0.0.	1.50	7.63	0. 0.	0.0.		1.7	0.65	1.9	2.2	1.0
Non- tan- nins	Per ct. 1.9	2.1	11.2.7.2 18.05 18.05		1.8	8 8 11 8 8		22.0	3.2	2.3 3.0 1.9	1.7	2.2
Uncom- bined tannin	Per ct. 2.9	3.1	94.99.99 81850		1.7	1.6			1.8	1.7 4.0 2.7	2.9	3.2
Degree of tan-nage	61.6	64. 6 64. 0	60.9 43.2 78.0 63.1		54.1	51.4		73.5	72.3	64. 4 62. 2 57. 8 56. 3	50, 5	75.2
Hide sub- stance	Per ct. 57. 5	56.7	57.8 55.5 49.9 57.8		61.2	62. 2 62. 9		47.6	48.0	57. 1 54. 0 54. 3 59. 7	61.2	52. 4
Com- bined tan- nin	Per ct. 35.4	36.6	38.55 38.58 36.58		33.1	32.0		35.0	34.7	36.8 33.6 33.6	30.9	39.4
Water sol- ubles	Per ct.	7.4. 2.4.	44.0.4.4		3.5	6. 6. 4. 4.		0.4. 0.8.	3.8	4.2.7.4.04.0	4.6	5.4
Petrol- eum ether extract	Per ct. 2.1	1.2	1.7.4.1.0 0.0.2.4	idi d	2.2	22.1		11.1	e. 6.		3.1	2.3
Insol- uble ash	Per ct.	66.63	ಬ್ಬಂದ ಬ	. e.	, n	ů. 4.		4.4.	r.4.	~0.∞v	.2	٠. تن
Total ash	Per ct.	4.73	04849	0.7.	۰ ۲	r. 8.		1.2	1.1		9.	1.0
Description	GOATSKIN LEATHER coat, sumac tanned, whole bind-	Law goat, sumac tanned, half binding 1- Crimison cape, whole binding, dull	Crimson cape, half binding, dull grain 1.  Natural Niger goat, dull scarlet  Red sumac goat  Green, hard grain, Morocco	Green Morocco, sumac tanned, peb- bled.	Brown Morocco, sumac tanned, smooth. Brown Morocco, sumac tanned, peb-	Blue Morocco, sumac tanned, smooth 1. Blue Morocco, sumac tanned, peb- bled.1	SHEEPSKIN LEATHER	Red roan  Law sheep, sumac tanned 1.  CALFSKIN LEATHER	Law calf. Blue calf, sumac tanned, whole bind-	Blue calf, sumac tanned, half binding 1.  Brown, bark calf Natural, bark calf Blue, sumac calf	COWHIDE LEATHER Red Russia	Red pigskin
Tan- ner	4	বৰ	4mm00	00	0 0	00		M4	M 4	4000	O	m
Leather	1	3.	5-6-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-	00-00-00-00-00-00-00-00-00-00-00-00-00-	11	1213		14 15	16	18- 19- 20- 21	22	23.

1 Labeled either "No mineral acids" or "Free from injurious acids."

## DISCUSSION

The acidity of the leather and the nature of the tanning material are naturally considered first. Thirteen of the 23 leathers were marked either "no mineral acids" or "free from injurious acids," and it is gratifying to find that of these 13 leathers, 9 had no acidity and the other 4 had only from 0.2 per cent to 0.3 per cent acidity. In other words, all the leathers so labeled were practically acid free, as determined by the Proctor and Searle method.

The acid content of the remaining 10 leathers was not specified. Of these only 3 had no acidity; 2 had an acidity of 0.5 per cent; and 5 had an acidity of from 1 to 2.2 per cent.

The data on hydrogen ion concentration and on acidity by the Proctor and Searle method afford a comparison of values for acidity by these two procedures. Kohn and Crede and others have suggested consideration of the selection of an initial pH value of 3.0 as the dividing point between safe and unsafe acidity for leather. The figures in the column for pH of water extract show that for leathers having an acidity of 0.5 per cent or less, as determined by the Proctor and Searle method, the pH value is appreciably greater than 3.0. The Kohn and Crede procedure, however, specifies 4.9 grams of leather per 100 milliliters of water, whereas the data given in Table 3 were obtained from extracts made on the basis of 1.6 grams of leather per 100 milliliters of water. Consequently, as these solutions were more dilute, they would be expected to give higher pH values. Because of the nature of these solutions, however, this increase would probably be very slight. On the other hand, the water digestion by the Kohn and Crede procedure is carried out at laboratory temperature, whereas the extractions in this case were made at 50° C., a difference in temperature which would result in more complete solution of extractable material and greater hydrolysis.

The results of these experiments also suggest that the nature of different classes of leather should be borne in mind in selecting a limiting pH value. Compared with heavy leathers, bookbinding leathers as a rule have a low content of uncombined material, and consequently they give a more dilute water extract.

Tests for the nature of the tanning material showed a predominance of the preferred pyrogallol tannage for durable bookbinding leathers. All the leathers marked "sumac tanned" were of a pyrogallol tannage, as were most of the others, even though the tannage was not specified.

In general, the leathers showed a tendency toward too high a degree of tannage, or overtannage, with its resulting tax on the "life" of the fiber. Five of the leathers had a degree of tannage of 70 or more;

<sup>&</sup>lt;sup>5</sup> Jour. Amer. Leather Chem. Assn., 18, 189 (1923); 20, 277 (1925).

7, a degree of tannage between 60 and 70; and 3, a degree of tannage between 55 and 60.

The petroleum ether extract, or what is commonly called the "fat" or "grease" content, was low in most of these leathers, particularly the goatskin leathers. Insufficient oil and grease is common in bookbinding leathers, a condition which is no doubt one of the contributory causes of the deterioration of these leathers. Leather bindings "starving for oil" are a familiar sight in nearly all libraries Most of the natural oils and greases of the skins are removed by the tanning operations. Failure to replace them is a severe handicap for the fiber of the leather, and even our best effort at restoration is but a poor substitute for nature's work. Oil must be incorporated in bookbinding leathers with caution because of the risk of producing a "greasy" effect and the consequent difficulties such a condition may present in the bindery. It would seem, however, from the recent developments in dressing, oiling, and fat liquoring, that satisfactory bindery-working leathers could be made containing from 5 to 10 per cent of oil or grease. Such a content of oil or grease of the best types would lengthen the life of the leather.

Most of these leathers, particularly those labeled "sumac tanned" and "free from injurious acids," comply substantially with the present chemical requirements for durable bookbinding leathers. The discussion of the data is offered not so much as criticism but more as suggestions that may be helpful in the production of even better leathers.

